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Speciation of uranyl sorbed at multiple binding sites on montmorillonite

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Abstract—We have investigated the structures of U (VI) complexes as uranyl moieties sorbed onto a reference montmorillonite, SAz-1, using X-ray absorption fine structure spectroscopy (XAFS) The uranyl-loaded clays were prepared from aqueous solutions of uranyl nitrate in the pH range from 3 0 to 3 5 The U concentrations on the clay ranged from 1 7 to 34 6% of the reported cation exchange capacity (CEC = 1 2 meq/g) of the clay For all samples, XAFS results indicate that there are two axial oxygen atoms at 1 78-1 80 Å, as expected for the uranyl moiety The average numbers and distances of equatorial oxygen atoms about uranyl sorbed on the clay vary significantly as a function of surface coverage At high coverage (34 6% CEC), the average number and distance of equatorial oxygen atoms are near those found for the fully hydrated uranyl species in aqueous solution However there are fewer equatorial oxygen atoms at a shorter average distance about uranyl sorbed at low coverage (1 7% CEC) At moderate coverage (7 3% CEC), the average number and distance of equatorial oxygen atoms are intermediate between those at higher and lower coverage These changes suggest that sorbing U is reacting with at least three different sites on the clay as U concentration increases The existence of multiple surface sites and sorption complexes which are structurally distinct from solution species need to be considered for rigorous modeling of sorption processes

INTRODUCTION

CONTAMINANT RELEASES that contain U are among the most serious problems that must be confronted by environmental restoration programs Plumes associated with mill tailings operations often have elevated levels of U and toxic metals with pore fluid pH values of 2-3 (MERRITT 1971) Uranium is also a principal metal contaminant in soils at Department of Energy weapon processing plants (RILEY and ZACHARA 1992) Under oxidizing conditions dissolved U is predominant in the U(VI) (uranyl) form (WEIGEL, 1986) and is quite mobile in the environment Recent studies have suggested that sorption of uranium onto oxides (JAFFREZIC-RENAULT et al 1980 YAMASHITA et al 1980 MAYA 1982 TRIPATHI 1984 HO and DOERN 1985, HO and MILLER 1985, 1986) and clay minerals (BOROVEC 1981, TSUNASHIMA et al, 1981 AMES et al, 1982 1983) may decrease U mobility in the environment

In an effort to predict U mobility, previous studies have proposed reactions governing sorption processes, based on surface measurements electrophoretic mobility, thermodynamic calculations spectroscopic data and properties of the solid The sorption complex has been suggested to form from a simple reaction between the solid surface and the predominant solution species For example, U sorption onto oxides is greatest at near-neutral pH values, and, in the absence of CO_2, $(UO_2)_3(OH)_5^+$ has been proposed as the sorbing species (HO and DOERN, 1985, HO and MILLER, 1985) HSI and LANGMUIR (1985) modeled the uptake of U by Fe oxides and hydroxides using two solution species, they proposed

that $UO_2(OH)^+$ forms a monodentate sorption complex and $(UO_2)_3(OH)_5^+$ forms most probably a bidentate sorption complex In contrast TRIPATHI (1984) successfully modeled uranyl sorption onto goethite assuming that the anionic species, $UO_2(OH)_3^-$ sorbs For carbonate-rich waters the anionic carbonato (DAVIES et al 1964) or hemicarbonato (HO and MILLER 1986) uranyl species is often thought responsible for U uptake YAMASHITA et al (1980) proposed that two anionic species $UO_2(OH)_3^-$ and $UO_2(CO_3)_3^{4-}$ sorbed to hydrous titania however they concluded that the same surface complex forms from sorption of both species

Rarely is the stoichiometry of the sorption complex determined directly Several studies conducted in carbonate-rich waters (DAVIES et al 1964 YAMASHITA et al 1980, HO and MILLER, 1986) have attempted to measure the carbonate-content of the sorbent or solution These authors concluded that the sorbing carbonate complex does not remain intact on the solid however these studies do not agree on the stoichiometry of the sorption complex

Defining the reaction stoichiometry implicitly involves identifying the reacting surface site Uranium strongly adsorbs to many oxide surfaces (MAYA 1982 HO and DOERN 1985), presumably bonding directly to the amphoteric sites in a chemical bond On clays two broad classes of sites have been identified crystallographically external amphoteric (edge) sites whose properties are pH dependent and fixed-charge (exchange') basal plane sites whose reactivity is thought to be independent of pH By analogy to results on oxides the U may sorb to the amphoteric sites on the surfaces of clays as a function of pH For clays the external surfaces contain coordinatively unsaturated edge sites, corresponding to nonbridging sites on oxide surfaces these unsaturated edge sites are thought to be much more reactive than saturated sites (SPOSITO, 1984) Because oxygen atoms on the basal planes of 2 1 clays (i e the siloxane surfaces) are fully

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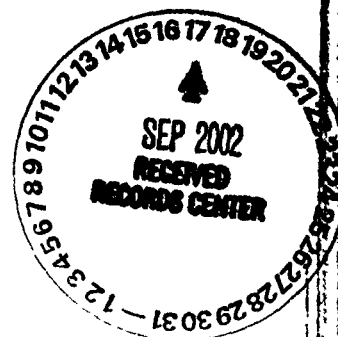
saturated they are not thought to protonate and deprotonate like amphoteric surface sites (SPOSITO, 1984) In contrast to the properties of the amphoteric sites, where specific chemical bonds may form, sorption to the exterior siloxane surfaces and exchange processes with interlayer cations are governed by electrostatics The dominance of electrostatics, in one case vs chemisorption, in the other may result in distinct sorption complexes at these different sites

Several studies have attempted to identify and differentiate these different sites and sorption mechanisms for uranyl species by chemical and/or spectroscopic means TSUNASHIMA et al (1981) and AMES et al (1982) argue that uranyl exchange with interlayer cations is the predominant sorption mechanism on smectites TSUNASHIMA et al (1981) report that Ca^{2+} release from the interlayer is similar to the U uptake by the clay, and infer that the interlayer cation was displaced by U TSUNASHIMA et al (1981) also argue that the linear uranyl moiety is oriented parallel to the basal plane of the clay based on the collapse of the interlayer spacing upon heating of uranyl-loaded montmorillonite AMES et al (1982) calculate an enthalpy of sorption (from the temperature dependence of U uptake) which is consistent with exchange reactions and not specific sorption SUIB and CARRADO (1985) argue that the two or three distinct luminescence lifetimes observed for uranyl-loaded clays are evidence for multiple sorption sites DENT et al (1992) argue that the XAFS spectra of uranyl sorbed to montmorillonite at moderate coverage is consistent with exchange of a uranyl carbonato complex into the interlayer However ZACHARA and MCKINLEY (1993) have successfully modeled uranyl sorption onto two different smectites as a combination of adsorption to two distinct amphoteric edge sites and exchange into the interlayer Recently, MORRIS et al (1994) deconvolved the composite emission spectra for uranyl sorbed onto montmorillonite into distinct spectral signatures where the number and ratios of these signatures are a function of uranyl coverage They conclude that this is evidence for at least four different surface complexes However the structures of the different complexes and surface sites were not discerned from these optical spectroscopic methods

The present study was undertaken to investigate the nature of U(VI) sorbed on clay from aqueous solution and specifically to discern changes in the uranyl sorption complex as a function of surface coverage X-ray absorption fine-structure (XAFS) spectroscopy provides explicit information about the local coordination sphere which may prove helpful in characterizing the uranyl sorption complex(es) To this end we have used XAFS spectroscopy to probe the structure of uranium sorbed on clay over a twentyfold range in coverage

EXPERIMENTAL

Materials

Uranium (VI) solutions were prepared by dissolution of recrystallized $UO_2(NO_3)_2$ $6H_2O$ (obtained from the Nuclear Material Technology Division of Los Alamos National Laboratory) in deionized water The initial pH of the U solutions used in the sorption experiments was adjusted to pH = 3 0–3 5 with HNO_3 or $Ca(OH)_2$ solutions prepared from ACS reagent-grade chemicals The montmorillonite used in this study was SAz 1 a reference smectite clay obtained from the Missouri Clay Source Repository SAz-1 has Ca^{2+} as the dominant exchangeable cation and a cation exchange capacity (CEC) of 1 2 meq/g (VAN OLPHEN and FRIPIAT 1979 AMES et al 1983)

Uranyl loaded clay samples were prepared by mixing SAz 1 (≈ 50 g/L) with uranyl solutions of different concentrations (0 51–46 6 mM) in polyethylene centrifuge tubes under ambient conditions (Table 1) The clay suspensions were mixed for 20–48 h The suspension were then centrifuged the supernatant removed and the solid rinsed several times with distilled deionized water The uranyl loaded clays were air-dried and lightly ground before being loaded into 2mm thick Al cells with mylar windows for XAFS data collection Final pH was measured for the supernatant in parallel experiments and varied from pH $\approx$ 3 4 (highest coverage) to pH $\approx$ 5 6 (lowest coverage) Uranium contents of the dried clay samples (Table 1) were determined using a kinetic phosphorescence analyzer (Chemchek Instruments Inc)

In addition to the clay samples XAFS data were collected for a 50 mM aqueous uranyl solution The aqueous solution was prepare as above with pH adjusted to 2 0 with HNO_3 at this pH and uranyl concentration the dominant solution species (>99%) is fully aquated UO_2^{2+} (GRENTHE 1992) The solution was syringed into an Al sample holder with mylar windows for XAFS data collection

XAFS Data Acquisition and Reduction

Spectra were obtained on beamline X8C at the National Synchrotron Light Source under dedicated operating conditions (2 5 GeV electron energy 110–220 mA stored current) Si [220] monochromator crystals were used detuned to remove harmonics by rotating the second crystal around the θ axis to lower the beam intensity ≈ 30–50% of its maximum Measurements were performed in the transmission mode Two to fourteen individual scans of each sample were collected and subsequently averaged during the data reduction process

Calibrations of the U L_{III}-edge were obtained simultaneously with the sample spectra or between samples by measuring the fluorescence from a slug of $U_{0.98}W_{0.02}$ alloy placed behind the second ion chamber the calibration standard and fluorescence detector were positioned relative to the second ion chamber such that fluorescence from the standard would not interfere with the sample signal The energy of the inflection point of the first feature in the spectrum of this standard was defined as 17167 eV the ionization threshold E_0 was set at 17185 eV from which k values were determined according to $k = [(2m/h^2)(E-E_0)]^{1/2}$ The edge was normalized by fitting polynomials through the pre-edge and XAFS regions and making the difference between the extrapolations of these polynomials unity at E_0 A three segment polynomial spline was fit to the region beyond the edge the difference between the data and this spline divided by

TABLE 1   Uranyl-loaded clay samples

Sample[a]	$[U]_{init}$	pH_{init}	$[U]_{tot}/[solid]_{tot}$	% uptake	pH_{final}	% CEC[b]
(mmol/g)	(mM)		(mol/g)			
0 208	46 6	3 0	9 814e-04	21 2	3 4[c]	34 60
0 044	4 98	3 5	9 704e 05	45 3	4 4	7 33
0 0103	0 506	3 0	9 898e-06	104 4	5 6[c]	1 72

[a] Sample name refers to the sorption density expressed as mmoles U sorbed per gram dry weight of clay
[b] Sorption density as % CEC assuming CEC = 1 2 meq/g
[c] Estimated from pH measurements for parallel experiments

the fall-off in the atomic absorption is the XAFS Two criteria used to determine the best spline were (1) that it minimized the amplitude of the Fourier transform modulus below $R = 1$ A, and (2) that it did so without changing the amplitudes of features at higher R (corresponding to actual components of the local structure) relative to split with fewer degrees of freedom, i e that the background was not overdetermined

Structural parameters for the first-coordination shells were obtained by curve-fits using empirical phase parameters derived from XAFS spectra of several solid uranyl compounds with known crystalline structures and empirical amplitude parameters derived from the spectrum for the aqueous uranyl solution [‡] The k^3-weighted raw data were first fit over the range $k \approx 2\ 2$–$11\ 5$ A^{-1}, the contributions of the axial and equatorial oxygens were each fit with a single shell, floating the uranium-oxygen (U-O) distance (R), the number of oxygen atoms (N) and the Debye-Waller factor (σ) for each shell The structural parameters (R, N and σ) for the axial oxygen shell were obtained from this fit

Information on atoms in the equatorial plane were extracted by a more involved procedure First the XAFS from the axial oxygens according to the first fit described above was subtracted from the raw data Because the XAFS is a sum of contributions from individual shells the residual contains the XAFS from the nearest neighbors other than the subtracted uranyl oxygen contribution this residual was Fourier transformed over the range $k \approx 2\ 5$–$8\ 5$ A^{-1} (using the closest nodes as end points) and then back-transformed over the range $R \approx 1\ 1$–$2\ 5$ A to obtain the Fourier-filtered XAFS spectrum due to only the equatorial oxygens This spectrum was subsequently curve-fit over the range $k \approx 3$–8 A^{-1} with a single U-O wave floating R and σ for that shell Because of the limited data range the number of atoms for this shell is reported as the integral of the overall amplitude $N \int dk \exp(-2k^2\sigma^2)$ relative to the aqueous solution [§] Reductions in the amplitude may therefore originate from either a reduction in N and/or an increase in σ for this shell The thermal contribution to σ will be Gaussian and increase with increasing R but will not change significantly over the range of bond lengths observed here However static disorder may produce a non-Gaussian distribution of U-O bond lengths which will result in the phase not being well-fit by a single shell of equatorial oxygen atoms Therefore the lack of a good fit of the phase by a single shell of equatorial oxygen atoms is diagnostic that static disorder contributes to a decrease in the amplitude

The errors in the structural information typically determined by curve fits of XAFS data are associated with (1) the quality of the data in terms of the signal-to-noise ratio and the success of the background removal process (2) the degree of the chemical (structural) correspondence between the actual system and the model compounds used to derive the parameters defining the XAFS [the amplitude mean free path radial distribution function (Debye-Waller terms for harmonic distributions) and change in the ionization threshold (ΔE_0)] and (3) the difficulty in uniquely determining those parameters that are correlated with one another

Assuming good data quality the accuracy of XAFS is customarily taken as $\pm 0\ 01$–$0\ 03$ A in the absorber-neighbor distances ± 15–2 in the numbers of neighbor atoms in a shell and ± 2–5 in the identification of the atomic numbers of the neighbor atoms These errors arise from the fact that although X-ray absorption is to first

order an atomic property certain parameters (e g the Debye Waller factor shift in the ionization threshold and loss terms) are nevertheless modified by the chemical attributes of the absorber Thus parameters derived from model compounds may not be identical to those of the unknown compound for which the parameters are used to fit the data It is clear however that the errors arising from the degree of the correspondence between model and unknown systems are systematic rather than random Therefore they can be substantially minimized by standardization using the XAFS of compounds of known structure closely related to the system being determined Such standardization also will diminish parameter correlation errors which originate from the fact that certain sets of parameters (e g the Debye-Waller factor and the number of atoms the shift in the ionization threshold and the absorber neighbor distance) although possessing different functional forms exert similar effects on the XAFS The effects of parameter correlation become more important as the data range is diminished This problem is ameliorated by fixing the values of certain parameters via the same standardization procedure used to set the phase shift and amplitude

In comparing the XAFS-derived structures of related systems where the XAFS parameters should be very similar or identical (i e the correspondence is quite high) a difference is essentially as significant as the data quality Thus the precision (as opposed to the accuracy) of an XAFS measurement can be sufficient to track easily a change from one chemical species to another For example we have observed changes in the Cu–O bonds in doped La₂CuO₄ of $0\ 02$ A in exact agreement with diffraction results (S D Conradson unpubl experimental results) and have followed the substitution of H_2O by NO_3^- in Pu(IV) complexes by tracking the second and third shell amplitudes with a precision of ca $0\ 2$ atoms out of four (VIERS et al 1992) Again using the fact that the structural parameters are derived from the full range of the data (albeit with increasing sensitivity as the range increases) our experience is that comparisons utilizing the qualities of the fits and the differences between the fits can validate differences of $< 0\ 01$ A in relative distance and < 5–10% in relative numbers of atoms in chemically similar systems An additional requirement to attain this level of precision is that the data being compared must be analyzed over the same range and in the same manner This is to avoid background subtraction Fourier filtering and fitting parameter artifacts since these operations are all dependent on the range of the data to which they are applied

RESULTS

The edge region of an XAFS spectrum can be very sensitive to subtle changes in the electronic and molecular structure of the central atom Thus although interpretation of its features may be difficult the edge is nevertheless a useful diagnostic for changes in the absorber environment The U L_{III}-edge spectra of the four samples under discussion, 50 mM aqueous UO_2^{2+} solution at pH = 2 0 and aqueous UO_2^{2+} sorbed on SAz-1 montmorillonite at 0 208, 0 044, and 0103 mmol U/g clay (Fig 1), all show the characteristic features of the uranyl moiety the broad white line peaking near 17178 eV and the shoulder at ≈ 17190 eV (PETIAU et al, 1984 FARGES et al 1992) Closer inspection shows a subtle narrowing of the width and apparent decrease in the height of the white line at the two lower loadings This observation suggests that the gross features of the local structure about uranyl will be conserved but that these complexes are not identical

Confirmation of this interpretation is given by the XAFS, shown in Fig 2 as the Fourier transform representation Fourier transformation produces a (phase-shifted) map of electron scattering density around the central atoms with each shell of atoms around the absorber contributing a peak in the transform modulus The peak position is related to the distance to neighboring atoms (R) and the peak amplitude

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[‡] Studies of the coordination about aqueous uranyl have concluded that there are either five (EVANS, 1963 ABERG et al 1983) or six (VDOVENKO, 1960 SHCHERBAKOV and SHCHERBAKOVA 1976) equatorial oxygen atoms Comparison of the amplitude of the XAFS for aqueous uranyl with the XAFS for an organic solution of uranyl nitrate in 20% tributyl phosphate/dodecane (C J Chisholm-Brause unpubl data), which is known to have six equatorial oxygen bonds (ULZ and NAVRATIL 1984) suggests that there are at least six equatorial oxygen atoms about uranyl in the pH = 2 005 M aqueous $UO_2(NO_3)_2$ solution

[§] The data range was limited as a result of an instrumental artifact that produced a medium-frequency glitch This glitch interfered with the higher frequency lower amplitude signal from the equatorial atoms at $k > \sim 8$ A^{-1}
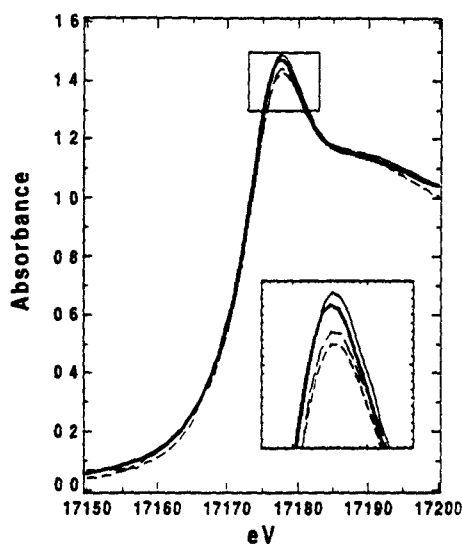
FIG 1 U L$_{III}$-edge spectra for (a) 50 mM aqueous solution pH 2 soln (——) and uranyl sorbed on montmorillonite at (b) 0 208 mmol clay (——) (c) 0 044 mmol clay (- -) and (d) 0 0103 mmol clay (---)

is related to the number of neighboring atoms (N) and the thermal and static disorder (σ) for that shell However the XAFS due to coordinating atoms with similar bond lengths will not be resolved into separate peaks in the Fourier transform representation

The large peak near $R \approx 1\ 3$ Å in all the spectra is the contribution from the axial oxygen atoms (Fig 2) its structure is essentially invariant which is consistent with known uranyl chemistry The next peak around $R \approx 1\ 9$ Å is the contribution from equatorial oxygen atoms which comprise the next nearest neighbor shell ca 0 6 Å farther from the U atom This peak exhibits a distinct decrease in amplitude at lower U loadings which indicates that the equatorial ligands are undergoing some type of change as conditions for uranyl sorption onto the clay are changed

To facilitate characterization of the equatorial shell the XAFS contribution from the axial oxygen atoms was removed from the spectrum by the procedure described in the experimental section, leaving the XAFS from the remainder of the structure (Fig 3) The XAFS from the equatorial oxygen shell was then further isolated by a Fourier filtering step (Fig 4) At this level changes in both the amplitude and phase among the samples are apparent The spectrum of the aqueous solution exhibits the largest amplitude the least damping of the amplitude with increasing k and the highest frequency indicating, respectively the largest number of atoms the smallest amount of disorder in the equatorial oxygen shell and the longest average U-O$_{eq}$ distance For the clay samples as the U loading decreases, the relative amplitude and frequency of the filtered XAFS decrease (Fig 4) which is consistent with a reduction in the number of equatorial atoms and/or an increase in disorder, and a decrease in the U-O$_{eq}$ bond length respectively

These interpretations of the data are corroborated by the curve fitting results (Table 2) For the sample with the highest uranyl loading (0 208 mmol/g) the U-O$_{eq}$ bond length is
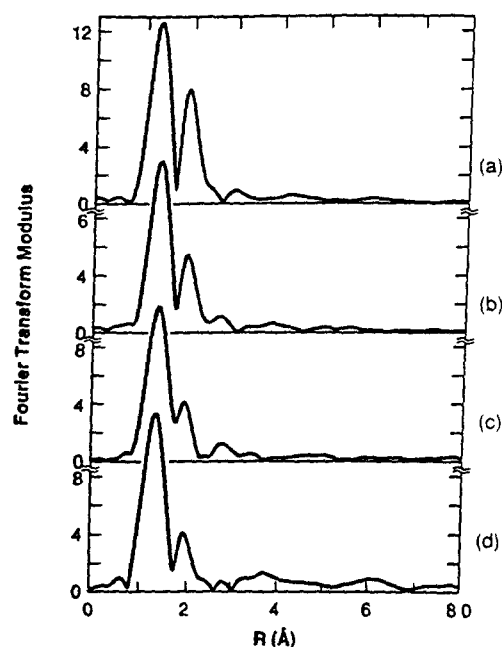

FIG 2 Fourier transform representation of the XAFS for the samples in Fig 1 Top to bottom (a) 50 mM aqueous solution pH = 2 0 and uranyl sorbed on montmorillonite at (b) 0 208 mmol U/g clay (c) 0 044 mmol U/g clay and (d) 0 0103 mmol U/g clay

0 016 Å shorter than in the aqueous solution with further reductions of 0 030 and 0 053 A as the loading is reduced by factors of 5 and 20 The overall amplitude reflecting both the number of atoms and the disorder also decreases mono-

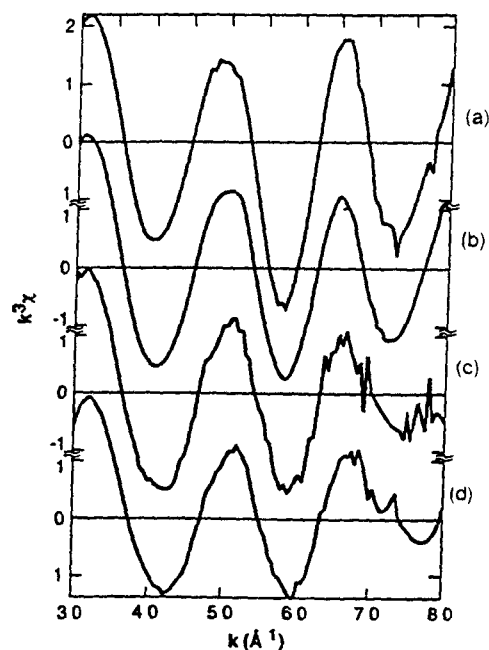FIG 3 Residual raw XAFS spectra for the samples in Fig 2 after the contribution from the axial oxygens was subtracted Top to bottom (a) 50 mM aqueous solution pH = 2 0 and uranyl sorbed on montmorillonite at (b) 0 208 mmol U/g clay (c) 0 044 mmol U/g clay and (d) 0 0103 mmol U/g clay
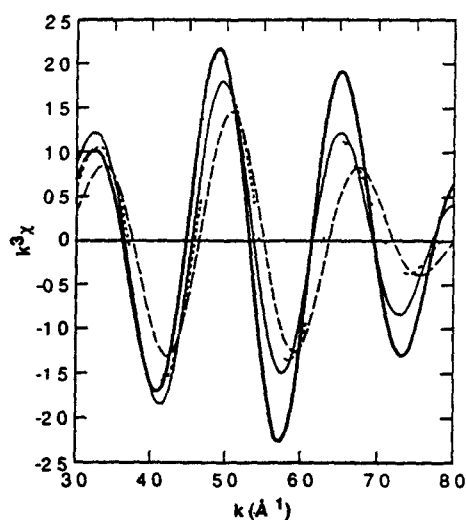
FIG 4 Comparison of the filtered XAFS spectra containing only contributions from the equatorial oxygen shell for the samples in Fig. 1 (a) 50 mM aqueous solution pH = 2 0 (———) and uranyl sorbed on montmorillonite at (b) 0 208 mmol U/g clay (———), (c) 0 044 mmol U/g clay ( ) and (d) 0 0103 mmol U/g clay (---)

torically to about 58% of its value in the solution sample at the lowest loading (0 0103 mmol/g)

As previously discussed an increase in disorder affects both the amplitude and phase of the XAFS The phase of the lowest coverage sorption sample (0 0103 mmol/g) is reasonably well-fit by a single coordination shell (not shown) This suggests that there is an actual decrease in the number of equatorial oxygen ligands relative to the aqueous solution However, the amount of the amplitude reduction (Table 2) and the small discrepancy between the phase of the fit and that for the data is consistent with greater static disorder as well The quality of the single shell fit is even worse for the 0 208 and 0 044 mmol/g samples, which is indicative of even greater static disorder in these samples This increased disorder could be due to a mixture of two or more sorption species, each having distinct U-O_{eq} distances or to large static disorder (U-O_{eq} distances which vary by $\geq$0 1 Å) in the equatorial plane of a single sorption species

The curve-fits also reveal some changes in the axial oxygen bond length an increase relative to the solution of 0 014 Å and 0 018 Å for the 0 208 mmol/g and 0 044 mmol/g samples, respectively, which returns to the solution value at the lowest loading (0 0103 mmol/g) Although small, these differences are within the <0 01 Å relative precision of the method suggesting that they are significant

DISCUSSION

The most significant finding from this work is the clear demonstration of a change in the local structure about U sorbed to montmorillonite as the surface coverage changes Specifically, as the surface coverage is decreased by a factor of from 0 208 to 0 044 mmol/g, there are fewer oxygen ligands in the equatorial plane at a shorter distance (2 444 Å vs 2 414 Å) As the surface coverage is further decreased to 0 0103 mmol/g, the number and distance of oxygen ligands in the equatorial plane about sorbed uranium further de-

crease The average number and distance of equatorial oxygen atoms for U in the intermediate coverage sample (0 044 mmol/g) are between that seen at higher and lower coverages However these results are not simply a mathematical average of the lowest and highest coverage species The axial oxygen shell of the 0 044 mmol/g sample is not intermediate between that for the 0 0103 and 0 208 mmol/g samples in fact, the U-O_{ax} distance is longest at intermediate coverage These results suggest that U forms at least three distinct sorption complexes on montmorillonite As XAFS provides only average structural parameters for sorbed U, it is difficult to ascribe structures to individual sorption complexes when the signal arises from mixtures of species However by accounting for changes in both the equatorial and axial oxygen shells about U we can determine the general characteristics of U sorbed on clay at different coverages

Note that the amplitude of the filtered XAFS function for the equatorial shell decreases as the frequency (i e , U-O_{eq} distance) decreases (Fig 4) A decrease in bond length concomitant with a decrease in coordination number is common in uranyl coordination chemistry On the basis of simple bond strength calculations (ZACHARIASEN 1976), the bond lengths determined in this study may be used to estimate the average equatorial coordination numbers in a manner that is independent of the XAFS determinations Specifically if the axial oxygen atoms are not involved in other bonds then the predicted equatorial oxygen coordination number for a U-O_{eq} distance of 2 391 Å 2 414 Å and 2 444 Å (corresponding to the average distance in the low medium, and high surface coverage samples) is $\approx$4 6 5 0 and 5 5 respectively (The predicted coordination number for the aqueous solution with U-O_{eq} = 2 460 Å is 5 7 near the value (6 0) estimated directly from the amplitude of the filtered XAFS function) These coordination numbers are 0 81 0 88 and 0 96 times the value for aqueous solution This is evidence that the large reductions in amplitude observed in the XAFS (relative amplitudes of 0 58 0 65 and 0 77, respectively) must be in part due to disorder and not solely to a reduction in coordination number

An equatorial coordination number of five is common for uranyl coordinated by monodentate ligands (EVANS 1963) The observed disorder may be within the equatorial shell of a single species by analogy to numerous uranyl compounds with five equatorial oxygen atoms at highly variable U-O_{eq} distances (e g uranophane, $CaUO_2(H_3O)_2(SiO_4)_2$ $2H_2O$, boltwoodite $KUO_2(H_3O)SiO_4$, bequerelite, $Ca[(UO_2)_6O_4(OH)_6]$ $8H_2O$ billietite, $Ba[(UO_2)_6O_4(OH)_6]$ $4H_2O$, and protasite $Ba[(UO_2)_3O_3(OH)_2]$ $3H_2O$ (STOHL and SMITH, 1981 PAGOAGA et al , 1987)) Alternatively, a predicted coordination number of about 5 may represent the average coordination number for several sorption species with 4, 5, and/or 6 equatorial oxygen atoms at distinct U-O_{eq} distances This latter possibility would also result in an apparent large disorder in the equatorial shell as observed in the XAFS

The predicted equatorial coordination number ($\approx$5) and the decrease in average U-O_{eq} distance for the two lower coverage samples suggest that equatorial ligands are lost upon sorption of at least some of the sorbing species at these coverages relative to uranyl in aqueous solution (Table 2) It is likely that uranyl sorbs to distinct surface sites whose

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TABLE II Structural information for the first-neighbor oxygen shells about uranyl in aqueous solution and sorbed on clay[a]

Sample	Axial Shell		Equatorial Shell	
	N	R (Å)	N_{ratio}[b]	R (Å)
50mM aq solution, pH=2 0	2 0	1 780	1 00	2 460
0 208 mmole U/g clay	2 0	1 794	0 77	2 444
0 044 mmole U/g clay	2 0	1 798	0 65	2 414
0 0103 mmole U/g clay	2 1	1 781	0 58	2 391

[a] The U O distances are typically accurate to ± 0 02 Å the precision for closely related structures is < 0 01Å The precision of the amplitude is typically 15 to 25%
[b] The ratio of the integrated amplitude ($\int dk\ N \exp(2k^2\sigma^2)$) of the sample to that of the uranyl solution

properties influence the local coordination about the sorbed U Furthermore the surface coverage at which a loss in equatorial ligands is observed (0 044 mmol/g or ≈7% CEC) is similar to the coverage (≈6-9% CEC) where TSUNASHIMA et al (1981) and M E Barr (pers commun 1992) report a change in the slope of a Langmuir-type plot of uranyl sorption on montmorillonite These results suggest that there are at least two distinct regions of uranyl sorption on montmorillonite below and above ≈7% CEC each region being dominated by sorption complexes with different local structures

The coincidence of a change in slope of the Langmuir-type plot of uranyl sorption and the appearance of a new sorption species implies discrete binding energies for these two species In general it is assumed that the most reactive sites are the first occupied by a sorbing species and thus it is likely that the uranyl complex formed at low coverages is taken up by a site to which it is tightly bound Furthermore the changes in coordination (i e loss of one to two coordinating ligands) imply that sorption at the lower coverages is not governed exclusively by electrostatics but rather that specific chemical reactions occur between the solution species and solid surface upon sorption

The two generic types of sorption sites identified on swelling clays (amphoteric edge sites and fixed-charge sites) probably have different affinity for aqueous uranyl and thus we might expect uranyl sorbed on these sites to be distinguishable These sites each constitute different fractions of the total number of available surface sites the pH dependent exchange capacity of clays which is an estimate of the number of available edge sites is generally about 5-15% of the total exchange capacity Thus it is possible that the sorption complex that forms up to about 7% CEC is bonding to edge sites of the clay Furthermore SPOSITO (1984) argues that edge sites on clays are most reactive for sorption

The proposed existence of a third sorption complex which is detectable only at low coverages (<0 0103 mmol/g) indicates that there is another subset of surface sites (which account for only a small fraction of the total available sites) which are occupied first at the lowest coverages These complexes may bond directly to the clay surface (i e as an inner-sphere complex) This specific sorption of uranyl to surface sites might allow for (if not require) the loss of equatorial ligands

This interpretation is consistent with data from ZACHARA and MCKINLEY (1993) who modeled uranyl sorption to montmorillonite as a combination of adsorption to three discrete sites two different amphoteric edge sites and fixed-

charge sites Sorption to edge sites was dominant at high cc - centrations of background electrolyte (i e conditions that suppressed cation exchange) and at higher pH values (ZACHARA and MCKINLEY 1993) In our experiments the Ca released into solution during equilibration of the clay was ~14-18 mM and Ca^{2+} has been shown to outcompete uranyl for fixed-charge sites on montmorillonite (BOREVEC 1981, TSUNASHIMA et al 1981) Thus exchange is expected to be suppressed for our lower coverage samples with higher equilibrium pH values In contrast the uranyl solution concentration of the highest coverage sample is much greater than that of Ca and the sorption density exceeds that estimated number of reactive edge sites Thus exchange into the fixed charge sites is expected under these experimental conditions

The sorption complex that forms at higher coverages is similar to the aqueous solution species which suggests that the local coordination sphere for this sorption complex is not strongly affected by sorption TSUNASHIMA et al (1981) and AMES et al (1982) argue that ion exchange governs uranyl sorption onto montmorillonite at these high coverages The similarity between the structure of the sorption complex and the aqueous uranyl species is also consistent with exchange into the fixed-charge sites Although monovalent cations (e g , alkali metals) in the interlayer of smectites lose part of their primary hydration sphere to form inner-sphere bonds at the siloxane ditrigonal cavities divalent cations in general are thought to retain their hydration sphere upon exchange (SPOSITO 1984) The d_{001} spacing of clays containing divalent cations is consistent with the presence of a cation surrounded by its primary hydration sphere (SPOSITO, 1984 MCBRIDE 1986) ESR studies of exchanged divalent cations also demonstrate that they retain their primary hydration sphere upon exchange (HARSH and DONER 1984 GOODMAN 1986, MCBRIDE, 1986) That the apparent amplitude of the filtered XAFS function for the equatorial shell is lower than it is for the solution sample probably indicates that the equatorial oxygen shell is distorted Note however, that these are air-dried samples and this distortion may be due in part to changes associated with drying The similarity of the $U-O_{eq}$ bond distance and shape of the XAS edge for the 0 208 mmol/g sample and aqueous solution suggests that uranyl sorbed at high coverages remains fully ligated as in aqueous solution but that the equatorial shell is distorted

CONCLUSIONS

This study demonstrates that structurally distinct U(VI) sorption complexes form on montmorillonite as a function

of coverage That the change in the slope of the Langmuir-type plot of uranyl uptake and the change in the structure of the sorption complex occur at comparable surface coverages is evidence that energetically different sites are involved in the sorption process This conclusion is consistent with luminescence studies that suggest that uranyl bonds to several distinct sites on clays (SUIB and CARRADO, 1985, MORRIS et al 1994) The differences between the dominant species at ≤7% CEC and those at higher coverages may reflect sorption onto amphoteric edge sites vs fixed-charge sites, respectively The differences in the XAFS results for the two low-coverage samples may also be attributable to the existence of two distinct sorption complexes on the edge sites However, these broad classes may not adequately account for all uranyl sorption in clays Further study is needed to determine if uranyl bonds directly to the clay surface at low coverages (analogous to sorption on oxides) The evidence presented here also argues strongly for the existence of sorption complexes that are structurally distinct from solution species Furthermore the uranyl sorption complexes which form at low coverages under conditions which are more typical of environmental problems, are the most distinct from those in aqueous solution Such results need to be considered in rigorous modeling of sorption processes

Editorial handling G Sposito

REFERENCES

ABERG M FERRI D GLASER J and GRENTHE I (1983) Structure of the hydrated dioxouranium (VI) ion in aqueous solution An X-ray diffraction and ¹H NMR study *Inorg Chem* 22, 3986–3989

AMES L L McGARRAH J E WALKER B A and SALTER P F (1982) Sorption of uranium and cesium by Hanford basalts and associated secondary smectite *Chem Geol* 35, 205–225

AMES L L McGARRAH J E and WALKER B A (1983) Sorption of trace constituents from aqueous solutions onto secondary minerals I Uranium *Clays Clay Mineral* 31 321–334

BOROVEC Z (1981) The adsorption of uranyl species by fine clay *Chem Geol* 32 45–58

DAVIES R V KENNEDY J MCILROY R W SPENCE R , and HILL K M (1964) Extraction of uranium from seawater *Nature* 203, 1110–1115

DENT A J RAMSAY J D and SWANTON S W (1992) An EXAFS study of uranyl ion in solution and sorbed onto silica and montmorillonite clay colloids *J Colloid Interf Sci* 150, 45–60

EVANS H T (1963) Uranyl ion coordination *Science* 141, 154–158

FARGES F PONADER C W CALAS G and BROWN G E JR (1992) Structural environment of incompatible elements in silicate glass/melt systems II U(IV) U(V), and U(VI) *Geochim Cosmochim Acta* 56, 4205–4220

GOODMAN B A (1986) Adsorption of metal ions and complexes on aluminosilicate minerals In *Geochemical Processes at Mineral Surfaces* (ed J A DAVIS and K F HAYES) *ACS Symp Series* 323, pp 342–361

GRENTHE I (1992) *Chemical Thermodynamics of Uranium* North Holland

HAM J B and DONER H E (1984) Specific adsorption of copper on an hydroxy-aluminum-montmorillonite complex *Soil Sci Soc Amer J* 48, 1034–1039

HO C H and DOERN D C (1985) The sorption of uranyl species on a hematite sol *Canadian J Chem* 63, 1100–1104

HO C H and MILLER N H (1985) Effect of humic acid on uranium uptake by hematite particles *J Colloid Interf Sci* 106 281–288

HO C H and MILLER N H (1986) Adsorption of uranyl species from bicarbonate solution onto hematite particles *J Colloid Inter Sci* 110, 165–171

HSI C -K and LANGMUIR D (1985) Adsorption of uranyl onto ferric oxyhydroxides Application of the surface complexation site binding model *Geochim Cosmochim Acta* 49, 1931–1941

JAFFREZIC-RENAULT N POIRIER-ANSRADE H and TRANG D H (1980) Models for the adsorption of uranium on titanium dioxide *J Chromatogr* 201, 187–192

MAYA L (1982) Sorbed uranium(VI) species on hydrous titania zirconia and silica gel *Radiochim Acta* 31, 147–151

McBRIDE M B (1986) Paramagnetic probes of layer silicate surfaces In *Geochemical Processes at Mineral Surfaces* (ed J A DAVIS and K F HAYES) *ACS Symp Series 323* pp 342–361

MERRITT R C (1971) *The Extractive Metallurgy of Uranium* Colorado School of Mines Research Inst

MORRIS D E CHISHOLM BRAUSE C J BARR M E CONRADSON S D and ELLER P G (1994) Optical spectroscopic studies of the sorption of UO₂²⁺ species on a reference smectite *Geochim Cosmochim Acta* 58, 3613–3623 (this issue)

PAGOAGA M K APPLEMAN D E and STEWART J M (1987) Crystal structures and crystal chemistry of the uranyl oxide hydrates bec querelite billietite and protasite *Amer Mineral* 72 1230–1238

PETIAU J CALAS G DUMAS T and HERON A M (1984) XAFS and edge studies of transition elements in silicate glasses In *XAFS and Near Edge Structure* (ed K O HODGSON et al) Vol 3, pp 291–296 Springer Verlag

RILEY R G and ZACHARA J M (1992) Chemical contaminants on DOE lands and selection of contaminant mixtures for subsurface science research DOE/ER 0547T U S Dept of Energy Office of Energy Research Washington D C USA

SCHULZ W W and NAVRATIL J D (eds) (1984) *Science and Technology of Tributyl Phosphate* Vol 1 CRC

SHCHERBAKOV V A and SHCHERBAKOVA L L (1976) Study of the solvation and complex formation of the actinides by the methods of NMR spectroscopy I Determination of the hydrate number of uranyl *Radiokhim* 18 207–210

SPOSITO G (1984) *The Surface Chemistry of Soils* Oxford Univ Press

STOHL F V and SMITH D K (1981) The crystal chemistry of the uranyl silicate minerals *Amer Mineral* 66 610–625

SUIB S L and CARRADO K A (1985) Uranyl clay photocatalysts *Inorg Chem* 24 863–867

TRIPATHI V J (1984) Uranium(VI) Transport Modeling Geochemical Data and Submodels PhD dissertation Stanford Univ

TSUNASHIMA A BRINDLEY G W and BASTOVANOV M (1981) Adsorption of uranium from solutions by montmorillonite compositions and properties of uranyl montmorillonites *Clays Clay Mineral* 29 10–16

VAN OLPHEN H and FRIPIAT J J (1979) *Data Handbook for Clay Materials and Other Non metallic Minerals* Pergamon

VDOVENKO V K (1960) *The Chemistry of Uranium and the Transuranium Elements* Acad Sciences USSR

VIERS D K SMITH C A ZWICK D D MARSH S F and CONRADSON S D (1992) Characterization of the nitrate complexes of Pu(IV) using absorption spectroscopy ¹⁵N NMR and EXAFS *J Alloys Compounds* (in press)

WEIGEL F (1986) In *Chemistry of the Actinide Elements* (ed J J KATZ et al) Chap 5 pp 169–442 Chapman and Hall

YAMASHITA H OZAWA Y NAKAJIMA F and MURATA T (1980) The collection of uranium from sea water with hydrous metal oxide II The mechanism of uranium adsorption on hydrous titania *Bull Chem Soc Japan* 53, 1–5

ZACHARA J M and McKINLEY J P (1993) The influence of hydrolysis on the sorption of metal cations by smectites Importance of edge coordination reactions *Aquatic Sci* 55, 250–261

ZACHARIASEN W H (1976) Bond lengths and bond strengths in compounds of the 5f elements In *Heavy Element Properties* (ed W MULLER and H BLANK) pp 91–95 North Holland Publishing Co